

Pyrolysis-Gas Chromatography/Mass Spectrometry of Polymeric Materials

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1. Introduction

Structural analysis and the study of degradation properties are important in order to understand and improve performance characteristics of synthetic polymers and copolymers in many industrial applications. Polymers/copolymers cannot be analyzed in their normal state by traditional gas chromatography (GC) because of high molecular weight and lack of volatility. However, by heating these macromolecules to temperatures above 500 °C, they are pyrolyzed into many individual fragmentation substances, which can be then separated chromatographically and identified by mass spectrometry.

Pyrolysis technique hyphenated to gas chromatography/mass spectrometry (GC/MS) has extended the range of possible tools for characterization of synthetic polymers/copolymers. Under controlled conditions at elevated temperature (500 – 1400 °C) in the presence of an inert gas, reproducible decomposition products characteristic of the original polymer/copolymer sample are formed. The pyrolysis products are chromatographically separated by using a fused silica capillary column and subsequently identified by interpretation of the obtained mass spectra or by using mass spectra libraries (e.g. NIST, Wiley, etc.). Pyrolysis methods eliminate the need for pre-treatment by performing analyses directly on the solid polymer/copolymer sample.

Most of the thermal degradation results from free radical reactions initiated by bond breaking and depends on the relative strengths of the bonds that hold the molecules together. A large molecule will break apart and rearrange in a characteristic way (Moldoveanu, 2005; Wampler, 2007; Sobeih et al., 2008). If the energy transfer to the sample is controlled by temperature, heating- rate and time, the fragmentation pattern is reproducible and characteristic for the original polymer. Another sample of the same composition heated at the same rate to the same temperature for the same period of time will produce the same decomposition products. Therefore the essential requirements of the apparatus in analytical pyrolysis are reproducibility of the final pyrolysis temperature, rapid temperature rise and accurate temperature control. Depending upon the heating mechanism, pyrolysis systems have been classified into two groups: the continuous-mode pyrolyzer (furnace pyrolyzer) and pulse-mode pyrolyzer (flash pyrolyzer) such as the heated filament, Curie-point and laser pyrolyzer. The pyrolysis unit is directly connected to the injector port of a gas chromatograph. A flow of an inert carrier gas, such as helium,

flushes the pyrolyzates into the fused silica capillary column. The detection technique of the separated compounds is typically mass spectrometry but other GC detectors have been also used depending on the intentions of the analysis (Sobeih et al., 2008). The currently commercially available pyrolysis equipment was described in detail in previous work of the author (Kusch et al., 2005).

The applications of analytical pyrolysis-gas chromatography/mass spectrometry range from research and development of new materials, quality control, characterization and competitor product evaluation, medicine, biology and biotechnology, geology, airspace, environmental analysis to forensic purposes or conservation and restoration of cultural heritage. These applications cover analysis and identification of polymers/copolymers and additives in components of automobiles, tires, packaging materials, textile fibers, coatings, half-finished products for electronics, paints or varnishes, lacquers, leather, paper or wood products, food, pharmaceuticals, surfactants and fragrances.

In earlier publications of the author (Kusch, 1996; Kusch et al., 2005), the analysis and identification of degradation products of commercially available synthetic polymers and copolymers by using analytical pyrolysis hyphenated to gas chromatography/FID and gas chromatography/mass spectrometry have been presented. In this chapter, examples of application of this analytical technique for identification of different polymeric materials are demonstrated.

2. Experimental

2.1 Instrumentation

Approximately 100 – 200 µg of solid sample were cut out with scalpel and inserted without any further preparation into the bore of the pyrolysis solids-injector and then placed with the plunger on the quartz wool of the quartz tube of the furnace pyrolyzer *Pyrojector II*[™] (S.G.E., Melbourne, Australia) (Figs. 1–2). The pyrolyzer was operated at a constant temperature of 550 °C, 600 °C or 700 °C. The pressure of helium carrier gas at the inlet to the furnace was 95 kPa. The pyrolyzer was connected to a 7890A gas chromatograph with a series 5975C quadrupole mass spectrometer (Agilent Technologies Inc., Santa Clara, CA, U.S.A.) operated in electron impact ionization (EI) mode. Two fused silica capillary columns (1) 60 m long, 0.25 mm I. D. and (2) 59 m long, 0.25 mm I. D. with *DB-5ms* stationary phase, film thickness 0.25 µm were used. Helium, grade 5.0 (Westfalen AG, Münster, Germany) was used as a carrier gas. The gas chromatographic (GC) conditions were as follow:

- (1) programmed temperature of the capillary column from 60 °C (1 min hold) at 7 °C min⁻¹ to 280 °C (hold to the end of analysis) and programmed pressure of helium from 122.2 kPa (1 min hold) at 7 kPa/min to 212.9 kPa (hold to the end of analysis),
- (2) programmed temperature of the capillary column from 75 °C (1 min hold) at 7 °C min⁻¹ to 280 °C (hold to the end of analysis) and programmed pressure of helium from 122.2 kPa (1 min hold) at 7 kPa/min to 212.9 kPa (hold to the end of analysis),
- (3) programmed temperature of the capillary column from 60 °C (1 min hold) at 7 °C min⁻¹ to 280 °C (hold to the end of analysis) and constant helium flow of 1 cm³ min⁻¹ during the whole analysis.

The temperature of the split/splitless injector was 250 °C and the split ratio was 20 : 1. The transfer line temperature was 280 °C. The EI ion source temperature was kept at 230 °C. The

ionization occurred with a kinetic energy of the impacting electrons of 70 eV. The quadrupole temperature was 150 °C. Mass spectra and reconstructed chromatograms (total ion current [TIC]) were obtained by automatic scanning in the mass range m/z 35 – 750 u. GC/MS data were processed with the *ChemStation* software (Agilent Technologies) and the *NIST 05* mass spectra library (Agilent Technologies).



Fig. 1. Pyrolysis-GC/MS system used in this work equipped with a furnace pyrolyzer *Pyrojector II*TM (S.G.E.), control module (S.G.E.), a 7890A gas chromatograph and a series 5975C quadrupole mass spectrometer (Agilent Technologies).

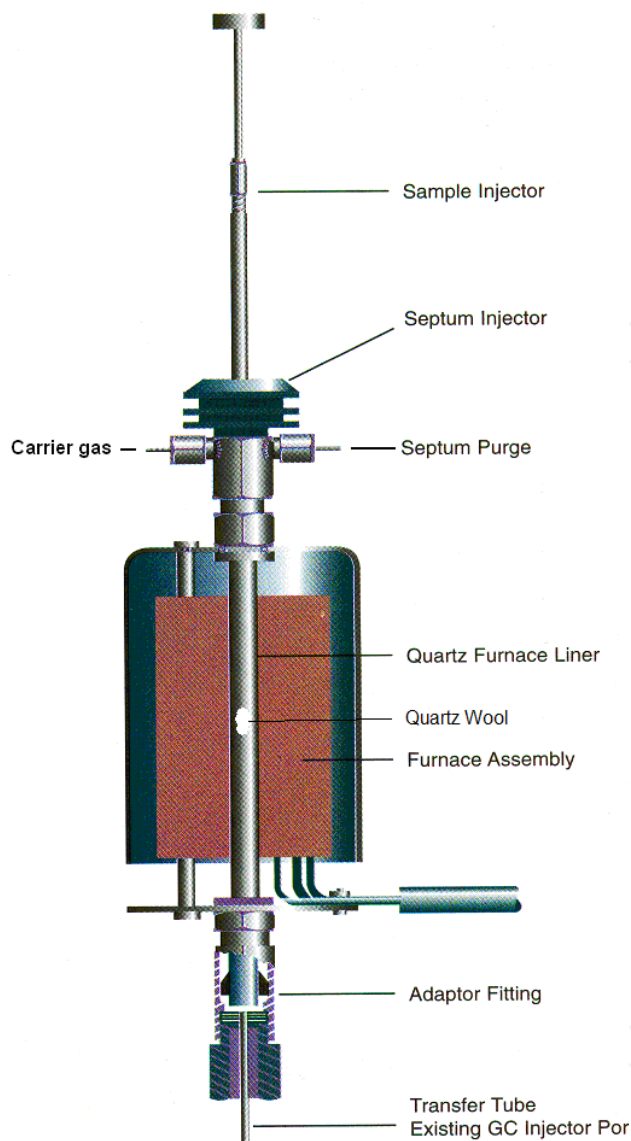


Fig. 2. Schematic view of the furnace pyrolyzer *Pyrojector II*[™] (S.G.E., Melbourne, Australia).

2.2 Samples

Samples of an unknown industrial plastic, a valve rubber, a car tire rubber, membranes of hydraulic cylinders from the automotive industry, an O-ring seal, dental filling material and recycled polyethylene were used in the investigation.

3. Results and discussion

3.1 Analytical pyrolysis of synthetic organic polymers/copolymers

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is used to characterize the structure of synthetic organic polymers and copolymers, polymer blends, biopolymers and natural resins. The traditional physical methods may only be applied to the analysis of technical organic polymers. Several chemical analysis techniques like UV-, FTIR- and NMR-spectroscopy, thermogravimetric analysis (TGA), size-exclusion chromatography (SEC, GPC), headspace-GC (HS-GC) or recently solid-phase microextraction (SPME) with GC/MS (Kusch & Knupp, 2002, 2004; Hakkarainen, 2008) have been established during the last four decades for characterization of macromolecules. These non-destructive methods offer information about functional groups, structural elements, thermal stability, molecular weight, and volatile components.

Pyrolysis-GC/MS is a destructive analytical technique. The most frequent use of this technique is the analysis of polymers and copolymers. Typical fields of interest and application (Hummel & Fischer, 1974; Hummel & Scholl, 1988; Hallensleben & Wurm, 1989; Moldoveanu, 2005; Kusch et al., 2005; Wampler, 2007) are:

- polymer identification by comparison of pyrograms and mass spectra with known references,
- qualitative analysis and structural characterization of copolymers, sequence statistics of copolymers, differentiation between statistical and block polymers,
- determination of the (micro) structure of polymers (degree of branching and cross-linking, compositional analysis of copolymers and blends, co-monomer ratios, sequence distributions, analysis of end-groups),
- determination of the polymers steric structure (stereoregularity, tacticity, steric block length, and chemical inversions),
- investigation of thermal stability, degradation kinetics and oxidative thermal decomposition of polymers and copolymers,
- determination of monomers, volatile organic compounds (VOC), solvents and additives in polymers,
- kinetic studies,
- quality control,
- quantification.

Starting at the University of Cologne (Germany) in the 1960s, Hummel and co-workers studied the process of thermal decomposition of polymers in detail using Py-GC/MS and Py-GC/FTIR (Hummel & Fischer, 1974; Hummel & Scholl, 1988). In general, decomposition proceeds through radical formation, which, due to the high reactivity of radicals, initiates numerous consecutive and parallel reactions. The authors summarized the main pathways of polymer decomposition in four categories:

1. retropolymerization from the end of the polymer-chain, predominantly forming monomers [e.g. poly(methyl methacrylate) (PMMA), poly-*n*-methylstyrene],
2. statistical chain scission followed by:
 - retropolymerization from radical bearing chain ends (e.g. polyisobutylene, polystyrene),
 - radical transfer and disproportionation (e.g. polyethylene, isotactic polypropylene),

- stabilization of fragments by cyclization (*e.g.* polydimethylsiloxane),
- 3. splitting side-chain leaving groups (*e.g.* polyvinylchloride, polyacrylonitrile, polyacrylate)
- 4. intramolecular condensation reactions with loss of smaller molecules (*e.g.* phenol-epoxide resins).

However, this classification is restricted to homogeneous polymers. The situation is more complex in copolymers, depending on the applied monomers and their linking (Hummel & Fischer, 1974; Hummel & Scholl, 1988; Kusch & Knupp, 2007).

In the following, practical application of the analytical pyrolysis connected to GC/MS for the identification of chemical structure and additives of an unknown industrial plastic, rubber products, dental filling material or recycled polyethylene will be presented. The possibility of using this technique in the failure analysis will be also demonstrated.

3.1.1 Identification of an unknown plastic sample

A sample of an industrial plastic was pyrolyzed at 600 °C and 700 °C, respectively in order to identify its composition. The total ion chromatograms (pyrograms) obtained for both pyrolysis temperatures were similar. Figure 3 shows the Py-GC/MS chromatogram of the sample pyrolyzed at 600 °C. Based on the decomposition products (Table 1), the plastic was identified as flexible poly(vinyl chloride) (PVC) with di-(2-ethylhexyl)phthalate (DEHP) plasticizer. The main features of the pyrolysis of PVC are the formation of hydrochloride (HCl) and the formation of unsaturated aliphatic and aromatic hydrocarbons. Benzene is the major pyrolysis product of PVC. Other aromatic components like toluene and the PAHs (polycyclic aromatic hydrocarbons) are also present (Table 1). This is the result of the formation of double bonds by the elimination of HCl from the PVC macromolecules, followed by the breaking of the carbon chain with or without cyclization (Moldoveanu, 2005). The formation of aromatic compounds in PVC pyrolysis is schematically exemplified for benzene in the same monograph (Moldoveanu, 2005).

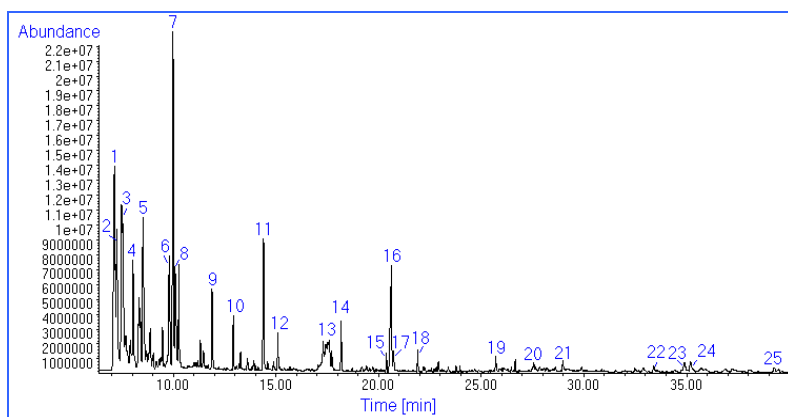


Fig. 3. Pyrolysis-GC/MS chromatogram of a plastic sample pyrolyzed at 600 °C, identified as flexible poly(vinyl chloride) (PVC). For peak identification, see Table 1. GC column 1, GC conditions 2.

The decomposition of the plasticizer di-(2-ethylhexyl)phthalate (DEHP) leads to the formation of 2-ethyl-1-hexene (RT = 9.98 min), 2-ethylhexanal (RT = 12.93 min), 2-ethyl-1-hexanol (RT = 14.40 min) and phthalic anhydride (RT = 20.63 min) (Table 1 and Fig. 3).

The obtained EI mass spectra of the compounds are shown in Fig. 4, while the chemical reaction of the thermal degradation of di-(2-ethylhexyl)phthalate is presented in Fig. 5. The reaction scheme is consistent with the previously published work (Bove & Dalven, 1984).

Peak	Retention time (RT) [min]	Pyrolysis products of polyvinyl chloride (PVC) with DEHP plasticizer at 600 °C
1	7.14	Hydrochloride/Propene
2	7.25	1-Butene
3	7.49	1,4-Pentadiene
4	8.05	2,4-Hexadiene
5	8.53	Benzene
6	9.81	Toluene
7	9.98	2-Ethyl-1-hexene
8	10.09	3-Methyl-3-heptene
9	11.89	Styrene
10	12.93	2-Ethylhexanal
11	14.40	2-Ethyl-1-hexanol
12	15.10	Indene
13	17.57	Benzoic acid
14	18.18	Naphthalene
15	20.38	2-Methylnaphthalene
16	20.63	Phthalic anhydride
17	20.73	1-Methylnaphthalene
18	21.91	Biphenyl
19	25.71	Fluorene
20	27.56	1,2-Diphenylethylene
21	28.97	Anthracene
22	33.45	Fluoranthene
23	34.89	Benzofluorene isomer
24	35.19	Benzofluorene isomer
25	39.35	Benz[a]anthracene

Table 1. Pyrolysis products of flexible polyvinyl chloride (PVC) with DEHP plasticizer at 600 °C. Peak numbers as in Fig. 3. GC column 1, GC conditions 2.

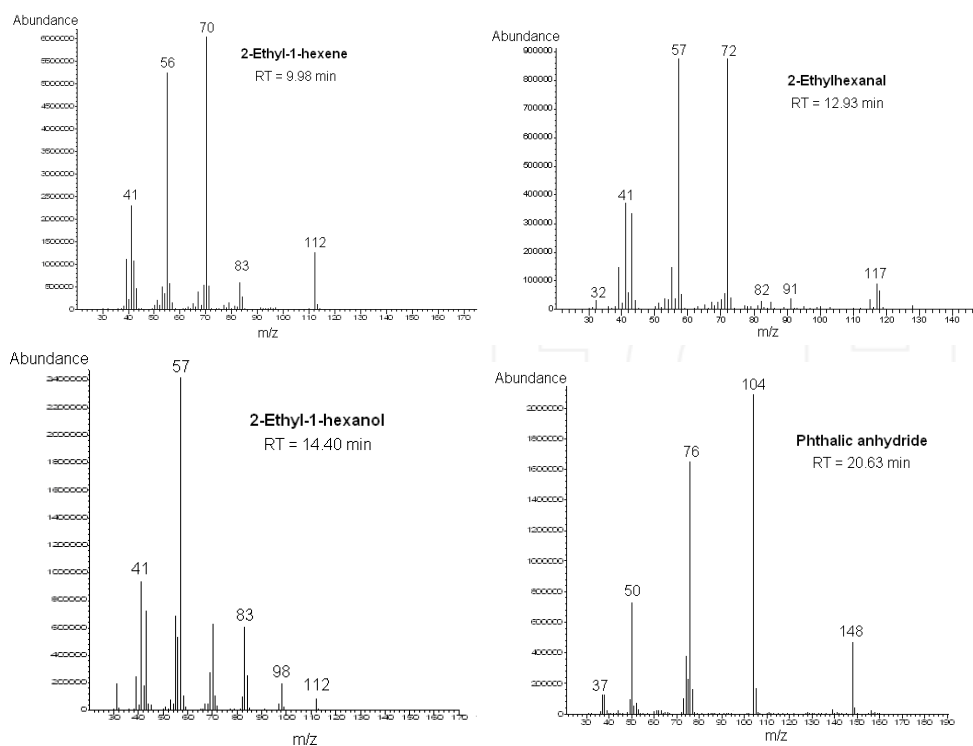


Fig. 4. EI ionization mass spectra at 70 eV of substances formed by the pyrolysis of the plasticizer di-(2-ethylhexyl)phthalate (DEHP) at 600 °C; RT = retention time of substance, as in Fig. 3 and in Table 1.

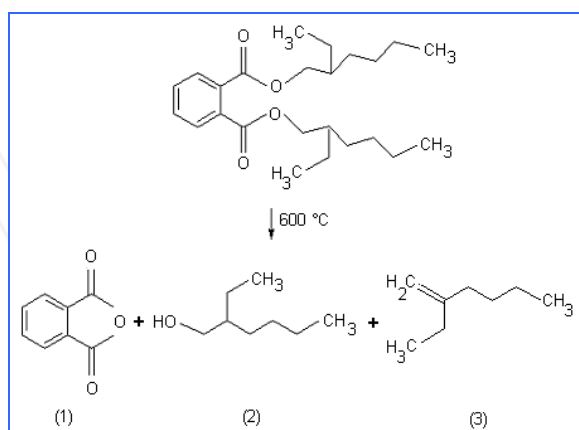


Fig. 5. Chemical reaction of the thermal decomposition of di-(2-ethylhexyl)phthalate (DEHP) at 600 °C leading to obtain (1) phthalic anhydride, (2) 2-ethyl-1-hexanol and (3) 2-ethyl-1-hexene.

3.1.2 Identification of rubber materials

The study of rubbers is the oldest application of analytical pyrolysis-GC (Kusch et al., 2005). Rubbers are frequently filled with opaque materials like carbon black, making them difficult for analysis by spectroscopy. Furthermore, cross-linking makes them insoluble and thus many of the traditional analytical tools for organic analysis are difficult or impossible to apply. Each rubber compound in a tire contains rubber polymers, sometimes one, but often a blend of two or more. The more commonly used polymers are natural rubber (NR, polyisoprene), synthetic polyisoprene (IR), polybutadiene (BR), and styrene-butadiene copolymers (SBR). SBR is widely used for tread compounds of a tire, generally in the tire treads of passenger cars, and NR in the relatively large-sized tires of buses and trucks etc. Inner tubes are usually based on butyl-rubber, a copolymer of isobutylene with a small proportion of isoprene.

Nitrile rubber (NBR) was invented at about the same time as SBR in the German program, in the end of the 1920s, to find substitutes for natural rubber (Graves, 2007). These rubbers are copolymers of acrylonitrile and 1,3-butadiene, containing 15 – 40% acrylonitrile. The major applications for this material are in areas requiring oil and solvent resistance. The largest market for nitrile rubber is in the automotive area because of its solvent and oil resistance. Major end uses are for hoses, fuel lines, O-rings, gaskets and seals. In blends with PVC and ABS, nitrile rubber acts as an impact modifier. Some nitrile rubber is sold in latex form for the production of grease-resistant tapes, gasketing material and abrasive papers. Latex also is used to produce solvent resistant gloves (Graves, 2007).

The criteria for assessing the quality of rubber materials are the polymer/copolymer composition and the additives. Commercial plastics and rubbers always contain a number of additives that are included to give particular physical and/or chemical properties. These additives include plasticizers, extender oils, carbon black, inorganic fillers, antioxidants, heat- and light stabilizers, tackifying resins, processing aids, cross-linking agents, accelerators, retarders, adhesives, pigments, smoke and flame retardants, and others (Hakkarainen, 2008).

The examined rubber materials in our laboratory were a valve rubber, a car tire rubber and an O-ring seal. On the one hand, based on the decomposition products at 700 °C (Fig. 6 and Table 2), the valve rubber was identified as a blend of polyisoprene (NR) and poly(styrene-*co*-butadiene) (SBR). On the other hand, the car tire rubber was determined as the mixture of polybutadiene (BR) and poly(styrene-*co*-butadiene) (SBR) (Kusch & Knupp, 2009).

Compounds, such as additives, are usually applied in low concentrations in plastic and rubbers. They are often recognizable as small irregularities within the characteristic pyrogram of the pyrolyzed material. By using the GC column 1 and the GC conditions 1, it was possible to identify the organic additives in both rubber samples. The peak of benzothiazole (Fig. 6, Peak 21, RT = 20.37 min) corresponds to the product of the thermal decomposition of benzothiazole-2-thiol (2-mercaptobenzothiazole, 2-MBT). In the rubber industry benzothiazole-2-thiol is used as vulcanisation accelerator and as antioxidant.

Furthermore, the antioxidant 2,6-bis-(1,1-dimethylethyl)-4-methylphenol (BHT) was detected in the pyrolyzate of the valve rubber (Fig. 6, Peak 29, RT = 25.50 min). The mass spectra obtained for both additives are shown in Fig. 7.

Peak	Retention time (RT) [min]	Pyrolysis products of the valve and the car tire rubbers at 700 °C
1	8.20	2-Butene
2	8.55	2-Methyl-1,3-butadiene
3	9.34	3-Methyl-2-pentene (isoprene)
4	9.75	5-Methyl-1,3-cyclopentadiene
5	10.08	Benzene
6	11.28	1-Methyl-1,4-cyclohexadiene
7	11.84	Toluene
8	13.51	Ethylbenzene
9	13.69	<i>p</i> -Xylene
10	14.08	Styrene
11	15.19	<i>m</i> -Ethyltoluene
12	15.52	<i>a</i> -Methylstyrene
13	15.81	1,2,4-Trimethylbenzene (pseudocumene)
14	16.28	1,2,3-Trimethylbenzene (hemimellitene)
15	16.78	Indene
16	17.43	<i>o</i> -Isopropenyltoluene
17	18.02	1,2,4,5-Tetramethylbenzene (durene)
18	18.75	3-Methylindene
19	18.86	2-Methylindene
20	19.58	Naphthalene
21	20.37	Benzothiazole
22	21.83	2-Methylnaphthalene
23	22.17	1-Methylnaphthalene
24	23.43	Biphenyl
25	24.06	Dimethylnaphthalene isomer
26	24.32	Dimethylnaphthalene isomer
27	24.43	Dimethylnaphthalene isomer
28	25.48	3-Methyl-1,1'-biphenyl
29	25.50	2,6-Bis-(1,1-dimethylethyl)-4-methylphenol (BHT)
30	26.52	1,6,7-Trimethylnaphthalene
31	27.75	Fluorene
32	29.88	1,2-Diphenylethylene (stilbene)
33	31.61	Anthracene
34	34.79	2-Phenylnaphthalene

Table 2. Pyrolysis products of the valve rubber and the car tire rubber materials at 700 °C. Peak numbers as in Fig. 6. GC column 1, GC conditions 1.

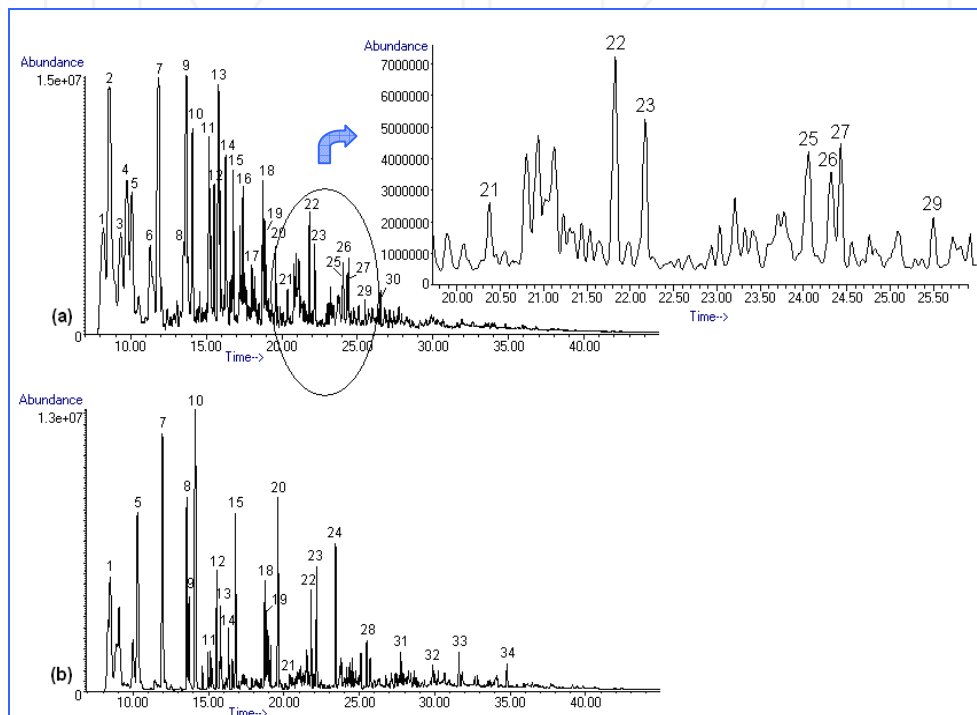


Fig. 6. Pyrolysis-GC/MS chromatograms (TIC) of the rubber materials at 700 °C; (a) NR/SBR, (b) BR/SBR. Peak 21 = benzothiazole (RT = 20.37 min), peak 29 = BHT (RT = 25.50 min). For other peak identification, see Table 2. GC column 1, GC conditions 1.

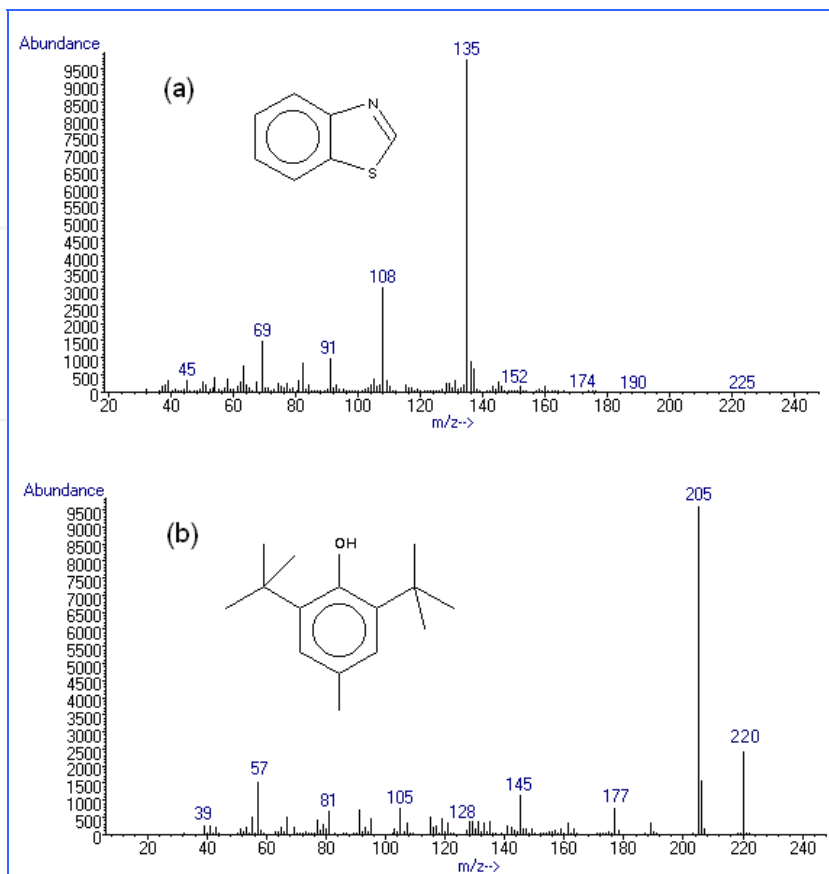


Fig. 7. EI mass spectra at 70 eV of the rubber additives pyrolyzed at 700 °C: (a) benzothiazole (thermal degradation product of benzothiazole-2-thiol), (b) 2,6-bis-(1,1-dimethylethyl)-4-methylphenol (BHT).

The pyrolysis-GC/MS chromatogram of the O-ring sample at 700 °C is shown in Fig. 8, while the identified degradation products are summarized in Table 3. Based on the decomposition products at 700 °C (Fig. 8 and Table 3), the O-ring rubber was identified as poly(acrylonitrile-*co*-butadiene) (NBR) with high content of the plasticizer di-(2-ethylhexyl)phthalate (DEHP) and with the vulcanization accelerator benzothiazole-2-thiol (2-mercaptobenzothiazole, 2-MBT). The analysis of pyrolyzate of poly(acrylonitrile-*co*-butadiene) indicated in Table 3 shows the presence of compounds generated from the acrylonitrile sequences (acrylonitrile, methacrylonitrile, benzonitrile), from the butadiene sequences (1,3-butadiene) and from the additives of the copolymer (2-ethyl-1-hexene, 2-ethyl-1-hexanol, phthalic anhydride and benzothiazol).

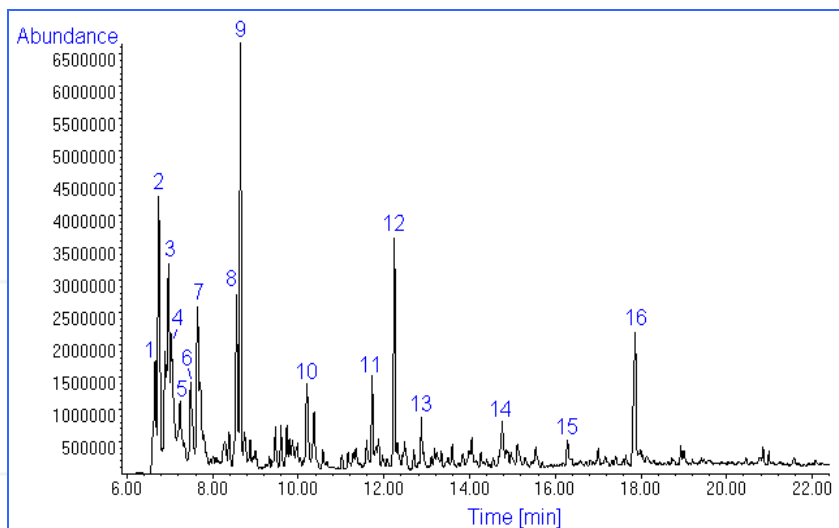


Fig. 8. Pyrolysis-GC/MS chromatogram (TIC) of the O-ring rubber at 700 °C identified as NBR with additives. For peak identification, see Table 3. GC column 2, GC conditions 2.

Peak	Retention time (RT) [min]	Pyrolysis products of the O-ring rubber at 700 °C
1	6.66	Propylene
2	6.74	1,3-Butadiene
3	6.97	Acrylonitrile
4	7.04	1,3-Cyclopentadiene
5	7.24	Methacrylonitrile
6	7.50	1,4-Cyclohexadiene
7	7.65	Benzene
8	8.56	Toluene
9	8.65	2-Ethyl-1-hexene
10	10.20	Styrene
11	11.73	Benzonitrile
12	12.24	2-Ethyl-1-hexanol
13	12.87	Indene
14	14.76	3-Methylindene
15	16.29	Benzothiazole
16	17.87	Phthalic anhydride

Table 3. Pyrolysis products of the O-ring rubber at 700 °C. Peak numbers as in Fig. 8. GC column 2, GC conditions 2.

3.1.3 Application of pyrolysis–GC/MS in the dentistry

A number of dental filling materials are presently available for tooth restorations. The four main groups of these materials, which dentists have used for about 35 years, are the conventional glass-ionomer cements, resin-based composites, resin-modified glass-ionomer cements and polyacid-modified resinous composites (Rogalewicz et al., 2006a). Light-curing glass-ionomer cements contain polyacrylic acid, chemically and/or photo-curing monomers (multifunctional methacrylates, like triethylene glycol dimethacrylate or 2-hydroxyethyl methacrylate), an ion-leaching glass and additives (initiators, inhibitors, stabilizers and others) (Rogalewicz et al., 2006a). Resin-modified glass-ionomer cements are now widely used in dentistry as direct filling materials, liners, bases, luting cements and fissure sealants (Rogalewicz et al., 2006b). These materials mainly consist of polymer matrix and glass-ionomer parts. The polymer matrix is based on a monomer system and different multifunctional methacrylates with additives (Rogalewicz et al., 2006b). Methacrylic monomers, like bisphenol A glycidyl methacrylate (Bis-GMA), urethane dimethacrylate (UDMA), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (HEMA) are the main components of resin-based dental filling materials. The presence of additives such as initiators, activators, inhibitors and plasticizers in uncured dental material mixture is necessary (Rogalewicz et al., 2006b).

Figure 9 shows the total ion current Py–GC/MS chromatogram of commercially light-curing dental filling material pyrolyzed at 550 °C. The pyrolysis products identified by using mass spectra library *NIST 05* are summarized in Table 4. The carbon dioxide (RT = 5.85 min) identified in pyrolyzate is formed from polyacrylic acid. The identified substances, like HEMA (RT = 13.65 min), EGDMA (RT = 19.48 min) and TEDMA (RT = 28.72 min) are known as standard composites of dental filling materials. Other compounds in Table 4, such as bisphenol A (RT = 33.10 min) or bisphenol A diglycidylether (RT = 42.42 min) are probably formed by thermal degradation of bisphenol A diglycidyl mono- or dimethacrylates. The presence of the additives, like antioxidant BHT [2,6-bis-(1,1-

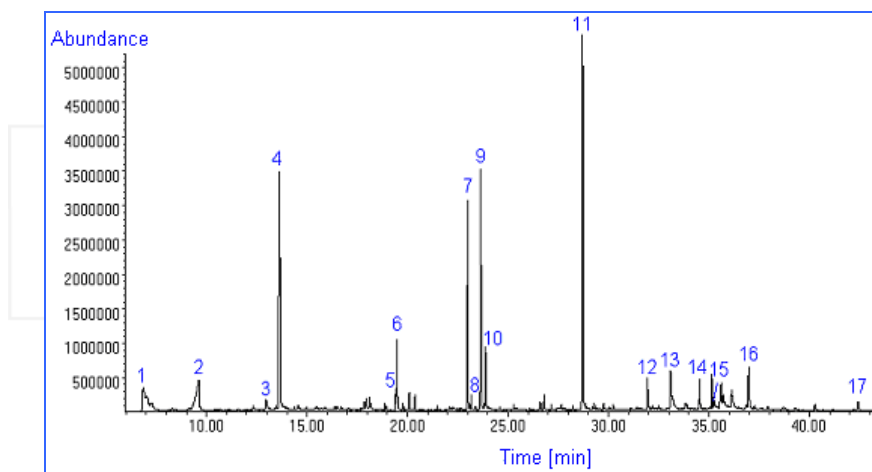


Fig. 9. Pyrolysis–GC/MS chromatogram of commercially light-curing dental filling material pyrolyzed at 550 °C. For peak identification, see Table 4. GC column 2, GC conditions 1.

dimethylethyl)-4-methylphenol, RT = 23.17 min] or the UV-absorber drometrizol (RT = 31.95 min) was also confirmed. The triphenylantimony (RT = 34.55 min) identified in pyrolyzate is used as catalyst in the UV-induced polymerisation.

Peak	Retention time (RT) [min]	Pyrolysis products of the dental filling material at 550 °C
1	5.85	Carbon dioxide
2	9.62	Methacrylic acid
3	12.96	Phenol
4	13.65	2-Hydroxyethyl methacrylate (HEMA)
5	19.40	4-Isopropenylphenol
6	19.48	Ethylene glycol dimethacrylate (EGDMA)
7	23.00	Not identified
8	23.17	2,6-Bis-(1,1-dimethylethyl)-4-methylphenol (BHT)
9	23.65	Not identified
10	23.89	Triethylene glycol (TEG)
11	28.72	Triethylene glycol dimethacrylate (TEDMA)
12	31.95	Drometrizol (Tinuvin-P, UV-absorber)
13	33.10	4,4'-Dihydroxy-2,2-diphenylpropane (Bisphenol A)
14	34.55	Triphenylantimony
15	35.25	Tetraethylene glycol dimethacrylate
16	36.98	4,4'-(1-Methylethylidene)-bis-[2,6-dimethylphenol]
17	42.42	Bisphenol A diglycidylether

Table 4. Pyrolysis products of commercially light-curing dental filling material at 550 °C. Peak numbers as in Fig. 9. GC column 2, GC conditions 1.

3.1.4 Environmental application of pyrolysis-GC/MS

Analytical pyrolysis has been used to study a variety of environmental samples including fossil fuel source rocks, natural resins or aquatic and terrestrial natural organic matter (White et al., 2004; Kusch et al., 2008a). Much work has been published on the analysis of soil (Tienpomp et al., 2001; Evans et al., 2003; Campo et al., 2011). Pyrolysis-GC/MS was also used in plastic recycling for analysis of products generated from the thermal and catalytic degradation of pure and waste polyolefins (Aguado et al., 2007).

Plastic recycling can be divided into mechanical (material) recycling, feedstock (chemical) recycling and energy recovery. In case of material recycling, the plastic waste is washed, ground and used in the plastic processing industry as a raw material. The chemical structure of the preserved material (re-granulate) is maintained. In case of chemical recycling, the residual polymers are converted catalytically into their monomers. The resulting monomers

are then used in the manufacture of new plastics. In the energy recovery the plastic waste is used in cement- or in steel industry as an energy carrier.

The following example presents that pyrolysis-GC/MS allows the identification of contaminants in low-density polyethylene (LDPE) re-granulate from mechanical recycling process. Figure 10 shows the obtained Py-GC/MS chromatogram of the LDPE pellets at 700 °C. The pyrogram consists of serial triplet-peaks of straight-chain aliphatic C₃–C₃₃ hydrocarbons, corresponding to α,ω -alkadienes, α -alkenes and *n*-alkanes, respectively, in the order of the increasing *n*+1 carbon number in the molecule. Such elution pattern is characteristic for the pyrolysis of polyethylene. For example, the triplet-peaks in Fig. 10 of C₁₀ hydrocarbons correspond to 1,9-decadiene (RT = 14.01 min), 1-decene (RT = 14.16 min) and *n*-decane (RT = 14.33 min), respectively. The identification of the compounds was carried out by comparison of retention times and mass spectra of standard substances, study of the mass spectra, and comparison with data in the *NIST 05* mass spectra library. The substances identified in pyrolyzate, like 2,4-dimethyl-1-heptene (RT = 11.12 min) and styrene (RT = 12.39 min) (Fig. 10) indicate the contamination of the recycled polyethylene with polypropylene and polystyrene, respectively. The detected palmitic acid (RT = 31.27 min) and oleic acid (RT = 33.99 min) suggest the presence of plant residues in the investigated re-granular material.

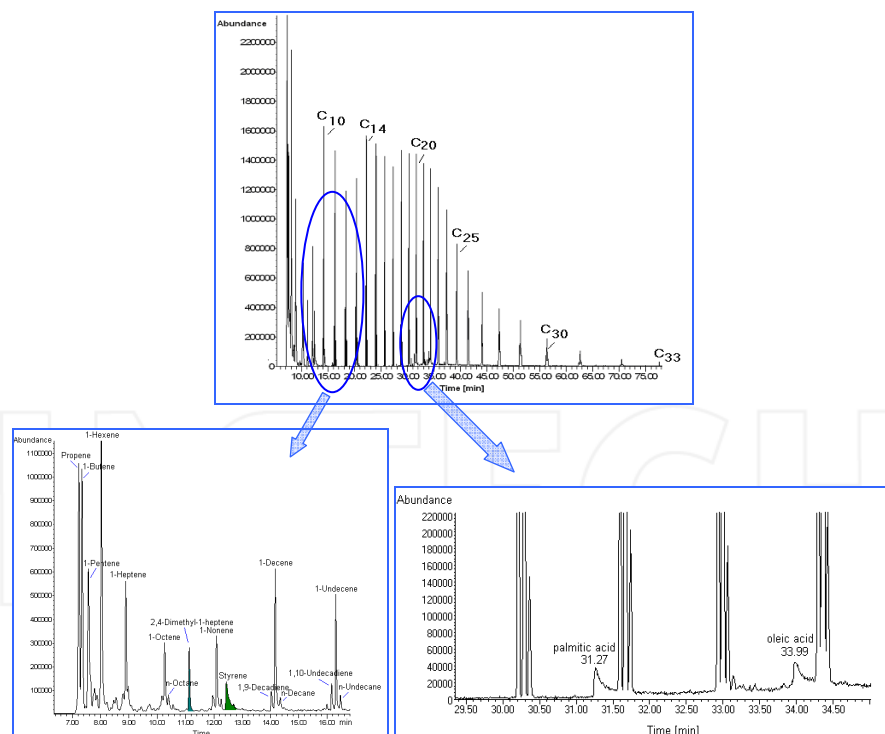


Fig. 10. Full view (top) and time windows between 6.2 – 16.8 min (bottom left) and 29.3 – 35.0 min (bottom right) of the Py-GC/MS chromatogram of recycled HDPE pyrolyzed at 700 °C. GC column 1, GC conditions 3.

3.1.5 Application of pyrolysis–GC/MS in the failure analysis

The increasing use of polymeric materials in the automotive industry requires sensitive and reliable methods for its analysis. For the failure analysis in motor vehicles there is often lack of information about the component itself, such as chemical composition, temperature resistance, possible contaminants or mechanical properties. The damage range is usually limited and not always homogeneous. There are often only small amounts of samples available to clarify the damage, which may be important for recognizing the cause of damage. Traditional analytical techniques used for characterization of polymers/copolymers, such as thermal analysis (TA) and Fourier transform infrared spectroscopy (FTIR) have limitations or are not sufficiently sensitive to demonstrate the change of the structure and the resulting dysfunction of used materials.

Previous work of the author (Kusch et al., 2008b) presents the application examples of Py-GC/MS in the failure analysis of various plastic or metal components and assemblies from the automotive industry. In the following case a glue residue on the surface of a rubber membrane from the hydraulic cylinder from the automotive industry was identified. Figure 11 shows the pyrolysis–GC/MS chromatograms at 700 °C, obtained from the new and operationally stressed rubber membrane coated with the glue residue, respectively.

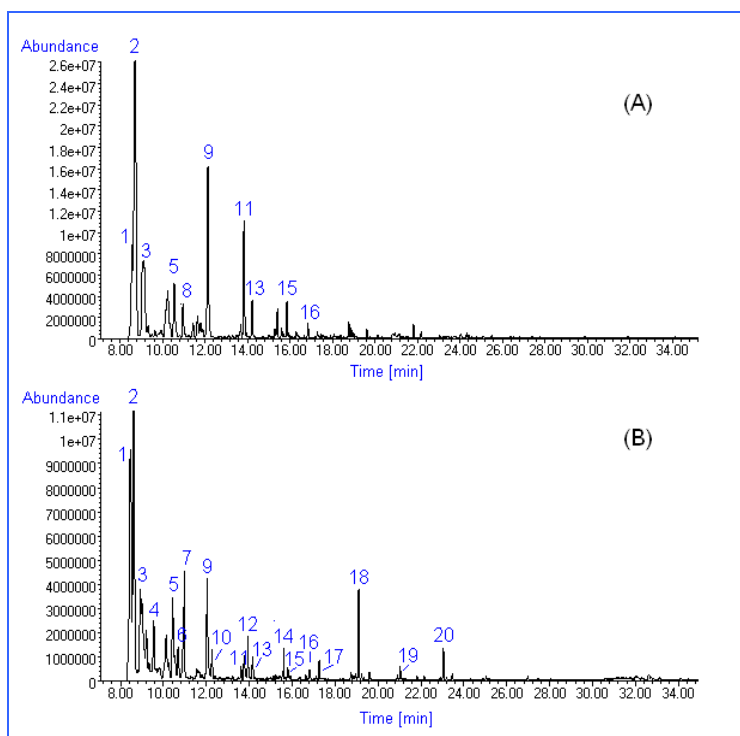


Fig. 11. Pyrolysis–GC/MS chromatograms at 700 °C, obtained from the new rubber membrane (A) and from the operationally stressed rubber membrane coated with glue residue (B). For peak identification, see Table 5. GC column 1, GC conditions 1.

The pyrolysis products identified by using mass spectra library *NIST 05* are summarized in Table 5. On the one hand, the pyrogram from the new rubber membrane obtained in Fig. 11 (A) consists of the characteristic fragments formed by the thermal degradation of poly(styrene-*co*-butadiene) (SBR). On the other hand, as can be seen from Fig. 11 (B) and from Table 5, the chemical structures of the identified substances of the operationally stressed rubber membrane coated with the glue residue build three groups of compounds: (1) *n*-alkenes and *n*-alkanes, (2) aromatics, and (3) ester. The presence of *n*-alkenes and heavy *n*-alkanes in pyrolyzate is characteristic for the pyrolysis of mineral oil (motor oil). The methyl methacrylate monomer (RT = 10.94 min) was produced by the retropolymerization of poly(methyl methacrylate) (PMMA) at 700 °C. Other peaks, like 1,3-butadiene (RT = 8.61 min), benzene (RT = 10.43 min), toluene (RT = 12.04 min), *p*-xylene (RT = 13.84 min), styrene (RT = 14.22 min), trimethylbenzene (RT = 15.87 min) and indene (RT = 16.85 min) are typical pyrolysis products of SBR. Based on the obtained results, it was possible to identify the glue coating from the surface of the rubber membrane from the automotive industry as a mixture of PMMA and mineral oil. The analytical results were then used for troubleshooting and remedial action of the technological process.

Peak	Retention time (RT) [min]	Pyrolysis products of the rubber membrane with glue coating at 700 °C	Pyrolyzed material
1	8.47	Propene	SBR, mineral oil
2	8.61	1-Butene/1,3-Butadiene	SBR, mineral oil
3	8.95	1-Pentene	Mineral oil
4	9.55	1-Hexene	Mineral oil
5	10.43	Benzene	SBR
6	10.72	1-Heptene	Mineral oil
7	10.94	Methyl methacrylate	PMMA
8	11.00	2,4-Dimethyl-1,3-pentadiene	SBR
9	12.04	Toluene	SBR
10	12.26	1-Octene	Mineral oil
11	13.84	<i>p</i> -Xylene	SBR
12	13.95	1-Nonene	Mineral oil
13	14.22	Styrene	SBR
14	15.56	1-Decene	Mineral oil
15	15.87	Trimethylbenzene	SBR
16	16.85	Indene	SBR
17	17.25	1-Undecene	Mineral oil
18	19.10	1-Dodecene	Mineral oil
19	21.04	1-Tridecene	Mineral oil
20	23.05	1-Tetradecene	Mineral oil
21	30.0 – 34.0	Heavy <i>n</i> -alkanes	Mineral oil

Table 5. Pyrolysis products of the rubber membrane with glue coating at 700 °C. Peak numbers as in Fig. 11. GC column 1, GC conditions 1.

4. Conclusions

Pyrolysis-GC/MS has proved as a valuable technique for the analysis and identification of organic polymeric materials in the plastic and rubber industry, dentistry, environmental protection and in the failure analysis. This technique allows the direct analysis of very small sample amounts without the need of time-consuming sample preparation.

5. Acknowledgements

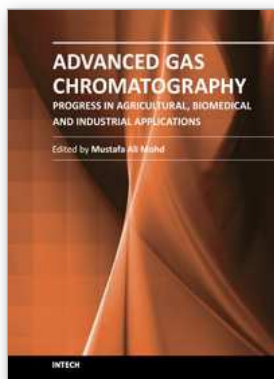
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Progress in agricultural, biomedical and industrial applications' is a compilation of recent advances and developments in gas chromatography and its applications. The chapters cover various aspects of applications ranging from basic biological, biomedical applications to industrial applications. Book chapters analyze new developments in chromatographic columns, microextraction techniques, derivatisation techniques and pyrolysis techniques. The book also includes several aspects of basic chromatography techniques and is suitable for both young and advanced chromatographers. It includes some new developments in chromatography such as multidimensional chromatography, inverse chromatography and some discussions on two-dimensional chromatography. The topics covered include analysis of volatiles, toxicants, indoor air, petroleum hydrocarbons, organometallic compounds and natural products. The chapters were written by experts from various fields and clearly assisted by simple diagrams and tables. This book is highly recommended for chemists as well as non-chemists working in gas chromatography.

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